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Characterization of Fine and Coarse Atmospheric Aerosols in Kuala Lumpur

M. Rashid,[1*] A. Rahmalan[1] and A. Khalik[2]

[1]Department of Chemical Engineering*
Universiti Teknologi Malaysia
80990 Johor Bahru, Johor, Malaysia

[1]Department of Chemistry
Universiti Teknologi Malaysia
80990 Johor Bahru, Johor, Malaysia

[2]Malaysian Institute for Nuclear Technology Research (MINT)
43000 Bangi, Selangor, Malaysia

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ABSTRAK

Sampel harian aerosol atmosfera (dalam tempoh Julai 1988 hingga Disember 1990) yang dipisahkan kepada zarahan halus (FP, aerodinamik diameter, d_a 2.5 μm) dan kasar (CP, $2.5 \leq d_a \leq 10$ μm) menggunakan *dichotomous sampler* telah dikumpul di Stesen Pensampelan Universiti Teknologi Malaysia, Kuala Lumpur. Sejumlah lapan belas kandungan unsur (Al, As, Br, Ca, Cl, Co, Fe, K, Mn, Na, Ni, P, Pb, S, Sb, Si, V, and Zn) telah ditentukan daripada aerosol tersebut. Secara purata, kepekatan keseluruhan unsur tersebut merupakan 19, 33, dan 23% daripada kandungan masing-masing FP, CP, dan TP (TP=FP+CP) dan lebih kurang 70% daripada kepekatan As, Br, K, Na, Pb, S, dan V ditemui dalam FP. Sementara S dan Si merupakan kandungan unsur utama dengan masing-masing menyumbang 61 dan 44% dalam FP dan CP. Berdasarkan kepada kajian pengkadaran sumber, tanah dan marin menyumbang 21 dan 5% daripada kandungan TP sementara bakinya 74% memerlukan kajian lanjut untuk penjelasan.

ABSTRACT

From July 1988 to December 1990 daily samples of atmospheric aerosols segregated into fine particlas, FP (aerodynamic diameter, d_a 2.5 μm) and coarse particles, CP (2.5 μm $\leq d_a \leq 10$ μm) were collected using a dichotomous sampler sited at the Universiti Teknologi Malaysia, Kuala Lumpur. Eighteen elements (Al, As, Br, Ca, Cl, Co, Fe, K, Mn, Na, Ni, P, Pb, S, Sb, Si, V, and Zn) were determined from the aerosol samples. On average, the total elemental concentration made up 19, 33, and 23% of the FP, CP, and TP (TP=FP+CP) fractions respectively, and approximately 70% of As, Br, K, Na, Pb, S, and V were found to be in the fine fraction. Both S and Si constituted the largest percentage of the total elemental concentration of 61 and 44% in the FP and CP fractions, respectively. Based on a source apportionment study, the soil and marine environments contributed 21 and 5% of the TP fraction while the remaining 74% of the aerosol concentration is yet to be explained.

Keywords: air pollution, aerosols, trace elements, source apportionment

INTRODUCTION

Atmospheric aerosols can be characterized by both their elemental composition and size distribution. Whitby *et al.* (1972) indicate that atmospheric aerosols fall into two distinct size classes: fine and coarse particles which result from different processes. Intensive attempts have been made to determine the chemical constituents of these aerosols in both urban and rural areas (e.g. Rahn 1976; Milford and Davidson 1985).

However, there have been few studies of trace elemental constituents of the atmospheric aerosols in the Kuala Lumpur area. Atmospheric lead (Pb) concentrations have occasionally been determined by local investigators but such studies have not been extended to other important trace elements. Rashid *et al.* (1986a) made the first attempt to analyse the multi-elemental composition of the total suspended particulate samples collected in the Kuala Lumpur area. Twenty-five elements were detected in the 18-day period of studies. The determination of the chemical constituents in precipitation samples in the area was reported by Lee and Low (1984).

The present study investigates the atmospheric elemental composition in two segregated aerosols collected over more than two years at the air quality monitoring station of Universiti Teknologi Malaysia in Kuala Lumpur. The aim was to scrutinize the characteristics of the elemental concentrations and their possible sources in both size ranges at the site.

METHODOLOGY

Sampling Site

The air quality station of Universiti Teknologi Malaysia is located 2 km northeast of the city centre of Kuala Lumpur (*Fig. 1*). The site has a mixture

Fig. 1. Location of the sampling site

of residential and commercial activities surrounded by various industrial estates within the Klang Valley Region (KVR). The KVR, with a population of about 3.0 million people, is the most densely populated and industrialized area in the country. It comprises a total area of about 3000 km^2 and includes the capital city of Kuala Lumpur, the largest and most important commercial centre in the country. Its climate is typical of the humid tropics, characterized by a uniformly high temperature with heavy annual precipitation.

Data Collection

The atmospheric aerosols presented in this work were sampled from July 1988 to December 1990. The daily (24 h average, midnight-to-midnight) inhalable fine aerosols (FP, with aerodynamic diameter, $d_a \leq 2.5$ μm) and coarse aerosols (CP, 2.5 μm $\leq d_a \leq 10$ μm) were collected using a Sierra Andersen automatic dichotomous air sampler (Model 244). The sampler was operated at 16.7 l min^1 with a sampling frequency of once a week. The sampler was placed on the roof-top of a building (*ca* 15 m height) at the Universiti Teknologi Malaysia campus. The flow rate of the sampler was routinely checked and calibrated using a calibrated rotameter. The reliability of the dichotomous sampler has been described with in detail by Briggs *et al.* (1982).

The fractionated fine and coarse aerosols were collected on 37-mm diameter membrane filters which were dried in a desiccator for at least 24 h before weighing. The filters were weighed in batches along with three control filters in order to avoid any erroneous gravimetric results (Neustadler *et al.* 1975). The gravimetric analysis of the filters was performed on a CAHN 30 microbalance equipped with an anti-static source to remove any strong electrostatic charge interference.

Elemental Analysis

A total of 139 segregated aerosol samples consisting of inhalable fine and coarse aerosols were collected and analysed for elemental composition in sequence using three different analytical techniques, X-ray fluorescence (XRF) spectrophotometer, neutron activation analysis (NAA), and atomic absorption spectrophotometer (AAS).

Potassium (K), phosphorus (P), sulphur (S) and silicon (Si) were analysed using the wavelength dispersive XRF machine (Philips Model PW1450) equipped with a computer control data processing facility. The XRF machine was operated at 60 kV 40 mA with fluorescence excitation accomplished by the chromium target X-ray tube. The characteristic X-ray emissions of K, P, S, and Si were detected and analysed by the gas flow counter detector and LiF(200) crystal, respectively. An analysing time of 40 s per element was observed for every filter sample. Similarly, the elemental contamination from the filter background was also determined using 20 blank filters.

A thin film standard was employed to calibrate the XRF machine (Giauque *et al.* 1974; Tominaga 1974). A series of metal solutions were prepared from high grade salt solutions of the element of interest (Raoof and Al-Sahhaf 1992).

The standard calibration curves were constructed for each element in terms of X-ray intensities against the standard elemental concentration per filter area within a given elemental concentration found in the actual aerosol samples. The reliability checks were made by comparing the X-ray intensities of freshly prepared known metal solutions of different concentrations against the calibration curve. Results from these reliability checks agreed to within ± 5% for all four elements.

The bulk of the elemental analyses in this study were performed by the NAA. Twelve elements were routinely detected; these included aluminium (Al), arsenic (As), bromine (Br), calcium (Ca), chlorine (Cl), cobalt (Co), magnesium (Mg), manganese (Mn), sodium (Na), antimony (Sb), vanadium (V), and zinc (Zn). The high background level of K and iron (Fe) in the filter substrate used in the study made it difficult to quantitatively determine these elements during the analysis. Therefore, the more reliable data of K and Fe from the XRF and AAS analysis were used for these elements, respectively .

The samples were neutron irradiated at an average neutron flux of 3×10^{12} n cm^{-2} s^{-1} (Reactor Triga Model Mk II at MINT, Bangi). The samples were placed in polyethylene tubes for irradiation. Measurement procedures and nuclear characteristics of the various radionuclides determined by NAA method have been reported (Dams *et al.* 1970). The gamma rays emitted by the nuclides in the radiated samples were detected by an HPGe detector connected to the Nuclear Data-66 multichannnel analyser and the computer code SAMPO-90 was used for spectra analysis (Nuclear Data, USA). Radionuclides were identified by their characteristic gamma ray energies after comparing them with the spectra of the standards, which were prepared by depositing mixtures of appropriate elements on a highly pure substrate (ashless filter paper) and sealing in polyethylene tubes. Standard concentrations were adjusted to make counting rates of the samples and the standards of comparable magnitude. Blank filters were also irradiated under the same treatments. The accuracy and precision of the NAA were verified by analysing the NBS reference materials of coal fly ash (SRM 1633a), tomato leaves (SRM 1573) and vehicle exhaust particulate (NIES No 8). The difference between the analysed and the certified values were in good agreement with the standard deviation on the analytical results range of 0.2 - 10% for Al, As, Ca, Mg, Mn and 1.8 - 17% for Br, Cl, Co, Na, titanium (Ti), V, and Zn.

Elemental Fe, nickel (Ni), and Pb were determined by the HGA-AAS (Perkin Elmer Model 5000). The sample was digested with 1.0 ml concentrated HNO_3 (BDH Analar) and heated in boiling water for at least 30 min to dissolve the residue. After cooling to room temperature, the sample was transferred and diluted with double distilled water in a 25-ml volumetric flask. The sample was analysed by the AAS together with the standard stock solutions (Fixanal, Germany). Blank filters were subjected to a similar treatment. Recovery studies of the elements using certified standard solutions found that the average recoveries of Fe, Ni, and Pb were 104, 107 and 102%, respectively.

RESULTS AND DISCUSSION

Elemental Concentration

The mean, standard deviation and ranges of the 18 elemental concentrations measured in the aerosol samples are presented in Table 1. The elemental concentration was corrected against repeated measurements of the filter blanks used in the sampling campaign. In general, the amount of aerosol mass deposited on the filter was small, which made it difficult to determine a wider range of elemental constituents. The total elemental concentration made up about 19, 33, and 23% of the FP, CP, and TP fractions, respectively. The remainder consisted mostly of organic or carbonaceous materials. Interestingly, in this study, a lower percentage of both was found in the CP than the FP fraction, confirming that organic materials are predominantly found in fine aerosols.

On average (Table 1) twelve elements (As, Br, Ca, Cl, Fe, K, Na, Ni, Pb, S, Sb, and V) were found to have higher or slightly higher concentration in fine than in coarse aerosols. This suggests that these elements are possibly related to anthropogenic sources which tend to concentrate in the finer fraction. The fine elemental concentrations of As, Br, K, Na, Pb, S, and V were at least twice as high as those in the coarse aerosols. The FP/CP elemental ratios of Ca, Cl, Fe, Mn, Ni, and Sb were between 1.0 and 1.80. The FP/CP ratios of Al, Co, Si, and Zn were found to be lower than 1.0 in this study, suggesting that these elements (though Co and Zn are exceptions) result from wind blown or earth surface abrasion which generates coarse particles.

The percentage of elemental concentration distribution in the FP and CP aerosols is shown in *Fig. 2*, which clearly indicates that As, Br, K, Na, Pb, S, and V are predominant in the fine aerosols in the area, representing about 70% of their concentration in this fraction. Most are known to be volatile and are usually deposited onto fine particles once released into the atmosphere. Likewise, the elements Al, P, and Si, concentrating in the coarse fraction, are non-volatile. On the other hand, in the study Mn was equally distributed in both fractions.

Sulphur constituted the highest percentage (50.3%) in the total elemental TP fraction, followed by Si (23.1%), K (7.70%), Na (6.30%), Ca (2.50%), Al (2.00%), Pb (1.90%), and P (1.80%). Similarly, a high percentage of S (61.0%) was found in the total elemental FP fraction with K, Si, Na, Ca and Pb constituting 10.0, 9.20, 8.60, 3.30 and 2.80%, respectively. As expected, Si represented the highest percentage (44.0%) in the total elemental CP fraction, followed by S (34.0%), Na (4.90%), K (4.80%), Ca (4.10%), Al (3.20%), and P (3.0%). The predominance of the elements in each size fraction indicates both their possible source and the importance of that source in the region.

Possible Elemental Sources

Although Ca, Fe, K, and Mn are known to be soil derived elements, their presence in the fine fraction is not unexpected. The presence of a very large

TABLE 1
Means, standard deviations, ranges of detectable elemental concentrations (ng m^{-3}) in Kuala Lumpur (1988-1990)

Element		N*	Mean	SD	Range			Method
Al	FP	124	91.9	77.0	21.0	-	614	NAA
	CP	129	129	101	10.0	-	515	
	TP**	137	204	131	10.0	-	646	
As	FP	116	5.96	6.56	1.11	-	58.0	NAA
	CP	106	1.10	0.59	0.04	-	4.58	
	TP	137	6.04	6.27	0.96	-	58.0	
Br	FP	129	25.4	16.5	1.00	-	74.0	NAA
	CP	107	6.49	5.50	0.50	-	27.0	
	TP	129	31.0	19.3	5.12	-	91.0	
Ca	FP	79	190	150	11.0	-	862	NAA
	CP	101	171	109	11.0	-	483	
	TP	121	266	198	11.0	-	1028	
Cl	FP	76	109	55.8	13.0	-	269	NAA
	CP	93	95.2	93.2	10.0	-	522	
	TP	107	106	135	10.0	-	709	
Co	FP	72	0.56	0.19	0.14	-	1.02	NAA
	CP	93	1.33	0.94	0.12	-	3.62	
	TP	115	1.43	1.02	0.24	-	4.08	
Fe	FP	96	91.5	52.8	13.0	-	260	AAS
	CP	98	51.9	52.3	10.0	-	232	
	TP	132	105	65.2	10.0	-	295	
K	FP	139	615	382	162	-	2709	XRF
	CP	130	187	99.7	17.0	-	486	
	TP	139	790	415	179	-	2803	
Mn	FP	90	5.18	4.92	0.23	-	33.0	NAA
	CP	62	5.15	4.81	0.54	-	33.0	
	TP	108	7.28	6.24	0.77	-	38.6	
Na	FP	137	484	247	23.0	-	1201	NAA
	CP	97	172	136	12.0	-	737	
	TP	138	601	278	43.0	-	1360	
Ni	FP	84	23.4	23.3	5.0	-	125	AAS
	CP	58	16.2	10.3	5.0	-	59.0	
	TP	104	27.9	23.9	5.0	-	125	
P	FP	133	68.6	142	10.0	-	1432	XRF
	CP	138	118	85.6	20.0	-	432	
	TP	139	183	157	30.0	-	1424	
Pb	FP	138	160	56.5	47.0	-	289	AAS
	CP	99	30.3	27.0	2.0	-	144	
	TP	139	181	57.9	2.0	-	320	

TABLE 1 (Cont'd)
Means, standard deviations, ranges of detectable elemental concentrations (ng m^{-3}) in Kuala Lumpur (1988-1990)

Element		N*	Mean	SD	Range	Method
S	FP	139	3865	1688	747 - 8559	XRF
	CP	135	1329	814	58.0 - 2915	
	TP	139	5156	1967	1348 - 11079	
Sb	FP	95	1.35	1.72	0.09 - 12.0	NAA
	CP	115	0.99	1.91	0.014 - 13.0	
	TP	136	1.78	2.28	0.09 - 15.5	
Si	FP	135	573	525	9.50 - 4932	XRF
	CP	139	2016	1684	97.0 - 8572	
	TP	139	2572	194	110 - 11038	
V	FP	139	1.12	1.95	0.04 - 19.0	NAA
	CP	112	0.35	0.48	0.014 - 4.79	
	TP	139	1.40	2.03	0.04 - 19.0	
Zn	FP	104	45.3	48.5	0.40 - 346	NAA
	CP	91	77.9	68.8	0.30 - 287	
	TP	135	87.4	96.2	0.30 - 633	

* N = number of samples with values detected above the filter blanks.
** TP = FP+CP, or TP equals the detectable size fraction concentration when one size fraction is not detectable.

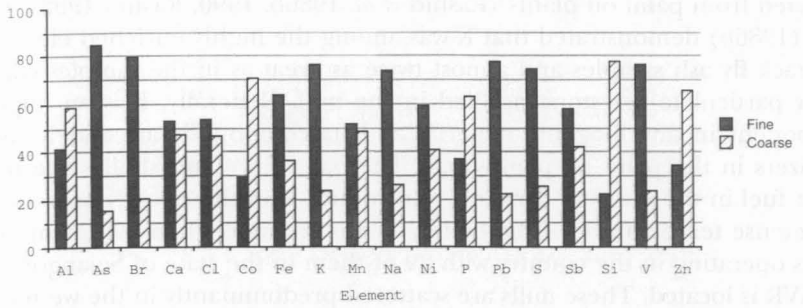

Fig. 2. Elemental concentration distribution in FP and CP aerosols

cement plant 25 km to the northwest of the sampling site could be a strong source of Ca in the area. In addition, Lee and Low (1984) reasoned that the high percentage of Ca in the rain-water collected in the region was not a natural occurrence, but due to human activities. Rashid *et al.* (1986a) found Ca slightly enriched in the suspended particulates compared to its crustal origin and assumed that Ca originated from soil. However, the existence of other sources of Ca was not discounted by the authors. The Ca/Si ratio of 0.33 in the FP aerosol fraction was slightly higher than the average crustal rock ratio of Ca/Si=0.13, supporting the idea of an anthropogenic origin of Ca in this fine

fraction. Although the concentration of Ca was relatively higher in the fine than the coarse aerosols, it was also widely detected in the coarse fraction where it is traditionally dominant.

The presence of Fe (64% of total Fe) in the finer fraction could be traced to smelting activities. There are as many as 109 iron and steel works/iron foundries (many of which are medium sized enterprises) scattered around the sampling site. These industries are located predominantly in the SW and SE quadrants of the sampling site. The biggest iron and steel industry in the region is located in the Shah Alam industrial estate, and it is a major source of fine Fe.

Mn could also be attributed to both natural and industrial emissions. The fact that Mn was more detectable in the FP than in the CP mass fraction suggests that it could be strongly linked to industrial source emissions. Pollutant emissions have been shown to enrich Mn in aerosol particles (Rahn 1981). A significant relationship between Mn and Zn (r = 0.48, p = 0.0001) in the FP fraction in this study suggests that there is a common source for these elements, such as the metallurgy/iron and steel industry. A positive correlation between Mn and Zn (r = 0.51) was also observed in previous studies (Rashid *et al.* 1986a). Therefore, it is most likely that these two elements have a common source in the area.

A substantial amount (10%) of the total fine elemental concentration is represented by K. The high concentration of K in this study was expected and can be attributed to the utilization of palm fibre and shell waste (as boiler fuel) in the palm oil mills as well as other biomass burning activities in the area. A high concentration of K has been reported in the mill boiler fly ash emissions collected from palm oil plants (Rashid *et al.* 1986b, 1990; Rashid 1992). Rashid *et al.* (1986b) demonstrated that K was among the highly enriched elements in the stack fly ash samples and almost twice as great as in the samples captured by air particulate arrestors installed in the mill. Generally, K is an important component in any biogenic material and its compounds are widely used as fertilizers in the palm oil plantations. The palm fibre and shell waste used as boiler fuel in the industry certainly reintroduce K in the stack emissions under the intense temperature of the boiler. There are more than 200 palm oil mill plants operating in the country with 29 of them in the state of Selangor, where the KVR is located. These mills are scattered predominantly in the western part of the state close to the shoreline. Thus, long range transport of K by local winds is likely to increase the K concentration at the site. The contribution of K from open burning, which is a common practice in the country, could also be substantial.

Lee and Low (1984) found that sea spray was the main source for chloride, sodium, and magnesium in the their studies of chemical composition in the rain-water collected locally. Similarly, it is possible that Cl and Na in this study are predominantly of marine origin. However, atmospheric Cl and Na aerosols associated with sea spray tend to dominate in the coarse fraction. Milford and Davidson (1985) reported that on average, 50% of Na and Cl are concentrated in particles larger than 3.8 μm and 3.0 μm, respectively. In contrast, in this

study, both Cl and Na were concentrated in the FP rather than the CP fraction. A similar observation of Cl and Na concentrating in the fine rather than the coarse particles at Dorset in central Ontario has been reported (Barrie 1988). One explanation given by the author was that many of the studies reported by Milford and Davidson were made closer to the sea where direct intrusion of Na and Cl produces larger particles than those at a distant site. Second, it is possible that the fine Na and Cl are the remnants of a marine aerosol with the largest particles lost during long range transport. The present authors take a similar view and in particular, that the ageing of the marine aerosol is much faster in a tropical than a temperate climate. Lower Cl/Na ratio of 0.22, 0.55 and 0.26 in the FP, CP and TP fractions, respectively, in this study compared to that in sea spray (Cl/Na = 1.8) illustrates that Cl (which is also more volatile than Na) is lost more rapidly than Na in the tropics.

It is well known that As, Br, Ni, Pb, S, Sb and V originate from various anthropogenic sources and their presence is strongly associated with specific source types. These elements are usually related to anthropogenic processes such as smelting and fuel oil combustion. Most are volatile or moderately volatile elements which are easily condensed on to fine particles in the atmosphere. Thus they are usually concentrated in ambient fine fraction aerosols (Natusch *et al.* 1974).

Automobile exhaust emissions are the main contributor of atmospheric Pb and Br in urban areas (Bowman *et al.* 1972). Lead is added in fuel as an antiknock agent while Br and Cl (in the form of ethylene dihalides) act as scavenging agents and are released together during the combustion of leaded fuel (O'Connor *et al.* 1977; Harrison and Sturges 1983). A significant relationship between Br and Pb ($r = 0.66$, $p = 0.0001$) in the fine fraction in this study (*Fig. 3*), is indicative of their common source and similar behaviour.

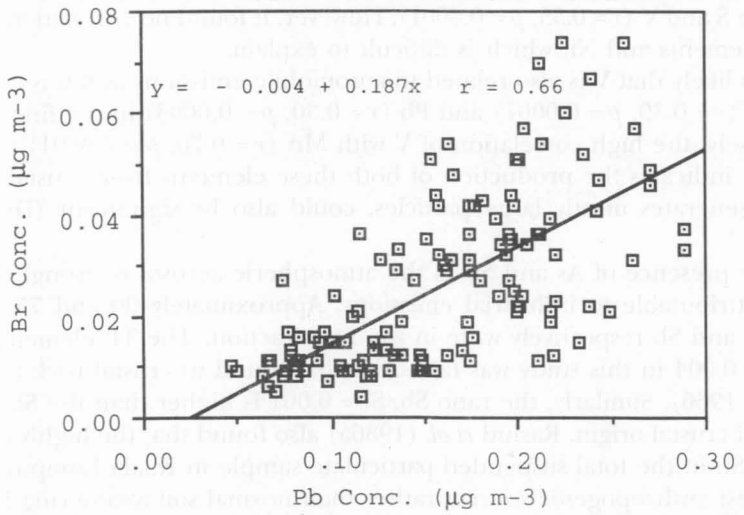

Fig. 3. Relationship of Br and Pb in FP aerosols

A similar strong relationship between Br and Pb at the same site has been reported by Rashid *et al.* (1986a). The positive relationship between Cl and Pb ($r = 0.35$, $p = 0.0017$) and Cl and Br ($r = 0.34$, $p = 0.0052$) indicates that the automobile is also responsible for Cl in the FP fraction. A lower correlation coefficient between Cl and Pb than Br and Pb suggests that Cl is more volatile than Br.

The overall mean concentration of Pb (in TP fraction) at the site is far below the recommended Malaysian guideline of 1.5 $\mu g\ m^{-3}$ (3-month moving average). At the time of the study, the maximum permitted level of Pb in petrol was 0.40 $g\ l^{-1}$ but this was reduced to 0.15 $g\ l^{-1}$ from January 1990. This reduction is reflected in the decrease in ambient Pb by almost 32% from 1989 to 1990 in this study. The introduction of unleaded petrol by two major oil companies, beginning in July 1990, also helped to reduce the atmospheric Pb levels, as was found in the study. However, the authors predict that this reduction will not last. The number of motor vehicles is increasing at the rate of 9% per year and thus increase in the consumption of leaded petrol will soon reintroduce Pb into the atmosphere at the same level as before. Nevertheless, the reduction of Pb in petrol does prove to have been effective.

Elemental Ni and V are two of the main elements associated with fuel oil combustion (Schmidt and Andren 1980). Fuel oil, which is the main type of fuel used by local industries, has a high sulphur content. Therefore, a high percentage of S in the fine fraction, along with Ni and V, could possibly be due to fuel oil combustion. The biggest power station in the country, located north of Port Klang about 30 km southwest of Kuala Lumpur, utilizes high sulphur content fuel oil ranging up to 3.2% S, which is probably the main source of these elements. In early 1990, a newly built 2×300 MW coal fired power station (which utilizes coal with 0.6% S content) started operating at the same power station and this could be another source for these elements. The study found positive correlation between S and V ($r = 0.35$, $p = 0.0001$). However, it found no correlation between these elements and Ni, which is difficult to explain.

It is likely that V is also related to automobile emissions as it was correlated with Br ($r = 0.39$, $p = 0.0001$) and Pb ($r = 0.30$, $p = 0.0003$) in the fine fraction. Conversely, the high correlation of V with Mn ($r = 0.70$, $p = 0.0001$) in the CP fraction indicates the production of both these elements from crustal erosion, which generates mostly large particles, could also be significant (Duce *et al.* 1983).

The presence of As and Sb in the atmospheric aerosol is strongly believed to be attributable to industrial emissions. Approximately 90 and 75% of the total As and Sb respectively were in the fine fraction. The TP elemental As/Si ratio of 0.004 in this study was far above that found in crustal rock 6.5×10^{-6} (Mason 1966). Similarly, the ratio Sb/Si = 0.001 is higher than the Sb/Si = 7.2×10^{-7} of crustal origin. Rashid *et al.* (1986a) also found that the highly enriched As and Sb in the total suspended particulate sample in Kuala Lumpur seemed to suggest anthropogenic sources rather than normal soil weathering for these elements. These findings strongly confirm that both elements are truly anthropogenic in nature.

The potential sources for As and Sb in the region are not fully understood. However, the large coefficients of variation (CV) for As (CV = 105%) and Sb (CV = 126%) in this study suggest that these elements are not uniformly distributed but strongly associated with localized sources. Rashid *et al.* (1986a) assumed that Sb could be attributed to a chemical factory which specializes in the manufacture of Sb related products. Pewter making and/or an electric-lamp filament manufacturing plants are possible sources for Sb in the area. SW and NE wind quadrants were found to be equally important in determining the Sb concentration at the site, each contributing 28% of the average Sb in the fine fraction. As much as 12.0 ng m^{-3} and 10.0 ng m^{-3} of Sb in the FP fraction were from the SW and NE quadrants, respectively. There is much mixed industrial activity in the SW quadrant and the potential sources for Sb could be numerous. A pewter making and a tyre remoulding plant could be two sources of Sb from the NE. The NE area is largely dominated by semi-conductor related industries which could also be a potential source for Sb. All these industries are located within 1-2 km of the sampling site and thus high Sb concentrations might be expected.

Similarly, it is difficult to relate As to any specific industrial source in the region. Its presence in the area can be attributed to many possible sources such as tin smelting operations, wood burning in the timber industry/ agricultural activities and other combustion related processes. Arsenic is known to be an effective ingredient used in the manufacture of herbicides or pesticides and wood preservatives, and thus will be emitted into the environment during burning of waste products in the agricultural and timber industry. A study of the trace element emissions from the stack of a local palm oil mill has shown that the concentration of As was six times higher in stack particulates than in residues collected in multiple cyclones (Rashid *et al.* 1986b). Many herbicides/pesticides are used in oil palm plantations and thus the use of palm fibres and shells as fuel in the plant would release residual As under the intense heat of the boiler. However, it is noteworthy in this study that the As/K ratio in the aerosol was 7 - 9 times higher than in the palm oil mill stack fly ash, suggesting that there are other potential sources of As in the area. Arsenic (together with Se) is enriched in the aerosol wherever coal is burned in quantity (Keeler and Samson 1988). Thus, the newly built 2 × 300 MW coal-fired power generation plant previously mentioned could be a potential source for As.

Al, Co, P, Si and Zn were found predominantly in the coarse fraction constituting 60-80% of the total elemental mass in the CP fraction. Co has been shown to have an average mass distribution of 2.63 μm (Milford and Davidson 1985), and its presence in the aerosol could be related to anthropogenic sources. The Co/Si ratio of 5.6×10^{-4} in the TP aerosol, which is 6 times higher than its crustal rock ratio, suggests that Co is anthropogenically related. This finding conforms with other studies (Rashid *et al.* 1986a).

The compounds of P are used in the production of fertilizers, detergents, insecticides, pesticides and special glass (Earl and Wilford 1991). The presence

of P in the aerosol could be related to these industries, especially from the fertilizer production sector. There are 66 chemical industries in the area which include fertilizer and pesticide related plants, mostly located in the SW quadrant of the sampling site. As much as 1424 ng m^{-3} of P in TP aerosol fraction with an average ratio of P/Si = 0.0712, which is 19 times higher than in its crustal rock origin, was observed from the SW wind quadrant. There was a significant correlation between P and K (r = 0.59, p = 0.0001) and P and Si (r = 0.56, p = 0.0001) in the coarse fraction, which suggests a common source for these elements, i.e. from fertilizer and soil components, respectively.

Zinc is known to be related to incineration or smelting processes and to concentrate predominantly in the fine fraction (Milford and Davidson 1985). However, in this study 63% of the total elemental Zn was found in the CP fraction. One possible explanation for this finding is that there may be a local source which contributes Zn to the coarse fraction at the site. Evidently, Rashid *et al.* (1988) found that Zn was highly enriched in the local urban road dust material and suggested that tyre wear (due to mechanical abrasion of tyres generating coarse particles) was the source of Zn in their findings. A similar explanation is given in this study.

Moreover, the higher mean Zn/Si ratio in all aerosol fractions of between 0.088 and 0.041 compared to that in their crustal origin (2.5×10^{-4}) illustrates that the Zn has an anthropogenic source. The positive correlation of Zn with Mn (r = 0.52, p = 0.0001) and of Zn with Co (r = 0.40, p = 0.0024) in the FP fraction suggests that all these elements have a common origin in the area. The seasonal variation of Zn concentration (*Fig. 4*) was consistent in both fractions, which also suggests that there is a specific local source for it. This source is probably related to high temperature processes since much more Zn was detected in the FP than the CP samples.

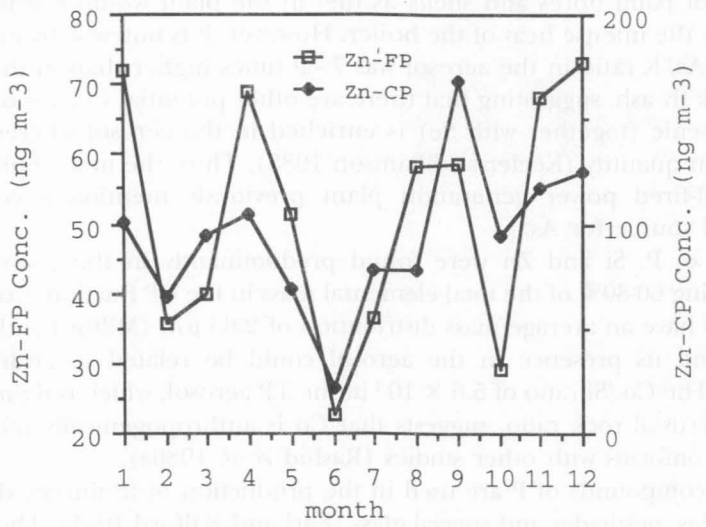

Fig. 4. Variability of Zn in FP and CP aerosols

Al and Si are the two main soil/crustal components and they are commonly used as normalizing elements to indicate whether an element is anthropogenically or naturally derived. Both have very limited pollution sources and a very high concentration in crustal rocks and soils. This makes them ideal for crustal reference elements (Rahn 1976). Since Al and Si are naturally derived, they are predominant in the coarse fraction of the atmospheric aerosol. The average coarse to fine ratios of Al and Si found in this study were 1.4 and 3.5, respectively.

As expected, these elements were positively correlated, with higher correlation coefficient in the CP ($r = 0.48$) than in the FP ($r = 0.26$) aerosol, which indicates the dominance of their source in the coarse fraction. Both showed a consistent seasonal variation during the study period. Both were also positively correlated with other known soil elements, such as K and Ca, in this study.

Naturally Derived Source Contribution

An attempt was made to estimate the contribution of two most important naturally derived aerosols, the soil and marine sources, in order to assess their impact at the site. At the same time, the anthropogenic source contribution was also estimated.

The non-crustal sodium aerosol, Na_{nc} (assumed to be of marine origin) and Si were used as the tracer elements for marine and soil origins respectively. The Na_{nc} was estimated by applying the following formula (Rahn 1981);

$$Na_{nc} = (Na)_{aero} - (Na/Si)_{crust} (Si)_{aero}$$

where Na_{nc} is the non-crustal origin or "excess" Na which is assumed to be of marine origin, $(Na)_{aero}$ and $(Si)_{aero}$ are the elemental Na and Si concentrations in the aerosol samples respectively, and $(Na/Si)_{crust}$ is the average crustal rock ratio of Na to Si, which is equal to 1.02×10^{-1} (Mason 1966). The marine contribution in each aerosol size fraction was determined by multiplying the ratio of Na_{nc} to its total elemental concentration by the aerosol concentration in each size fraction. The same approach was used to calculate the soil contribution of Si in the aerosol samples.

Table 2 presents the estimated average soil and marine source contributions as well as the unexplained aerosol mass (which represents sources other than soil and marine) at the sampling site. On average, soil contributes 21, 33.6 and 9.0% in the TP, CP and FP aerosol fractions, respectively. As expected, soil contributes a much larger percentage in the CP than in the FP fraction. Conversely, soil contributes relatively a small percentage to the FP aerosol fraction. The marine source contributes 5.0, 4.8, and 7.8% of the TP, CP, and FP aerosol fractions, respectively. Notably, this contribution is shown to be quite consistent in all aerosol size fractions, which indicates the suitability of Na_{nc} as a tracer element for this source.

Interestingly, the unexplained aerosol concentration contributes a higher percentage mass to the FP (83.2%) than the CP (61.6%) fraction. This

TABLE 2
Average soil, marine, and unexplained source contributions* in Kuala Lumpur

Source/ Aerosol	TP	Min - Max	CP	Min - Max	FP	Min - Max
Soil	10.3	0.90 - 29.8	5.59	0.57 - 20.5	3.28	0.04 - 16.2
(%)	(21)	(1.5 - 46)	(33.6)	(4 - 68)	(9.0)	(0.1 - 28)
Marine	2.34	0.04 - 8.43	0.79	0.01 - 3.25	2.47	0.08 - 6.77
(%)	(5.0)	(0.1 - 14)	(4.8)	(0.2 - 15)	(7.8)	(0.2 - 24)
Unexplained# aerosol mass	37.1		7.84		29.7	
(%)	(74)		(61.6)		(83.2)	
Average aerosol mass	49.7		14.2		35.5	

* Contribution in $\mu g\ m^{-3}$.
(%) = Percentage contribution.
Unexplained mass = Average aerosol mass - (soil + marine).

concentration represents the anthropogenic sources, carbonaceous and organic materials, as well as secondary pollutants such as the by-products of photochemical activities. Thus, it is not surprising that most of this aerosol mass is in the fine fraction. Moreover, the unexplained aerosol contributes a consistently high concentration to the FP fraction, with a range of 70 - 86%, compared to 25-83% in the CP fraction.

Both soil and marine source contributions showed a marked seasonal variation at the site (*Fig. 5*). The soil source contribution reached 29.8 $\mu g\ m^3$ during a high pollution day in August, contributing 45.6% of the TP aerosol concentration. The marine source contribution seemed to be influenced by the surface wind speed, particularly during the beginning of the intermonsoon (October) and during the northeast monsoon periods (January). During these months wind speeds were much higher (20-30%) than the annual average. The maximum percentage of marine contribution was as high as 12 - 14% of the TP aerosol at the site. Woodcock (1953) also reported that the production of sea-salt particles increased with wind speed.

As a comparison, Table 3 presents the percentage contribution of soil and marine sources in the TP fraction found in this study with other source apportionment studies in the area. The study of Rashid and Griffiths (1994) was based on factor analysis with the multiple linear regression approach while the Japan International Cooperation Agency (JICA 1993) study was based on the chemical element mass balance receptor model. Both studies were based on

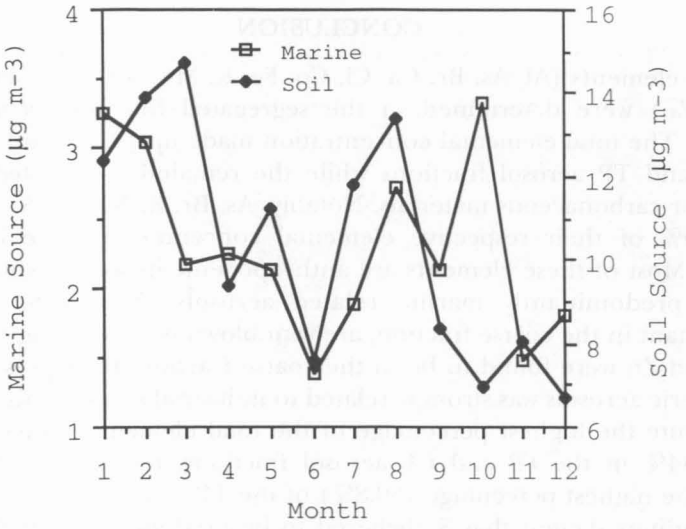

Fig. 5. Contribution of marine and soil in TP aerosol

TABLE 3
Comparison of estimated marine and soil contributions from source apportionment studies in Kuala Lumpur

Source	Rashid & Griffiths (1994)	JICA (1993)	This work
Marine	8.3%	3.0%	5.0%
Soil	11.6%	3.5%	21.0%
Total naturally derived aerosols	19.9%	6.5%	26.0%

Note: total naturally derived aerosols = Marine + Soil.

airborne trace element concentrations sampled on rather a small number of days (less than 15 days).

As shown in Table 3, the estimated average range of soil and marine contributions in the Kuala Lumpur area was 3.5 - 21% and 3.0 - 8.3% respectively. The total naturally derived aerosol contribution (i.e. soil + marine) in the area was 6.5 - 26.0%. The JICA results yielded a lower estimate of the contribution of naturally derived aerosols than the results of the present study, which show that the naturally derived aerosols contribute quite significantly (26%) to the ambient TP aerosol concentration in the area. In contrast, the results of the present work agree with those obtained by Rashid and Griffiths in their source apportionment studies, despite the use of different approaches.

CONCLUSION

Eighteen elements (Al, As, Br, Ca, Cl, Co, Fe, K, Mn, Na, Ni, P, Pb, S, Sb, Si, V, and Zn) were determined in the segregated fine and coarse aerosol fractions. The total elemental concentration made up 19, 33, and 23% of the FP, CP, and TP aerosol fractions while the remainder consisted mostly of organic or carbonaceous materials. Notably, As, Br, K, Na, Pb, S, and V, with about 70% of their respective elemental concentrations, are in the fine fraction. Most of these elements are anthropogenic in source whilst Na (and Cl) are predominantly marine related aerosols. Al and Si, which are predominant in the coarse fraction, are windblown or of soil origin. Although Co, P, and Zn were found to be in the coarse fraction, their presence in the atmospheric aerosols was strongly related to industrial source emissions. S and Si constitute the highest percentage of the total elemental concentration of 61 and 44% in the FP and CP aerosol fractions, respectively. Similarly, S showed the highest percentage (50.8%) of the TP elemental aerosol fraction. These findings suggest that S (believed to be predominantly in the form of $SO_4^=$) results from secondary pollution which plays an important role in fine aerosol formation in the region.

A simplified source apportionment approach carried out in this study revealed that soil contributes 21, 33.6 and 9.0% in the TP, CP, and FP fractions. Marine sources contribute quite consistently in all size fractions (4.8 - 7.8%). The combined contribution of the naturally derived aerosols (soil + marine sources) is 26% in the TP aerosol concentration. The remaining 74% of the aerosol concentration reflects other source contributions and is yet to be identified.

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